of orbital (and state) correlations are just as real in excited states as they are in ground states. Even if the deactivation step leading to products actually proceeds through the V–O minimum,[3] that minimum cannot be reached if such a barrier intervenes, unless sufficient extra energy is available.

We wish to propose that the requirement of "extra energy" in photochemical reactions in dense media may be much more common than is currently realized. Experimentally, it may give rise to (a) temperature-dependent quantum yields, (b) wavelength-dependent quantum yields, (c) triplet reactions requiring a sensitizer of disproportionately high T_1 energy, (d) two-photon reactions ($S_0 + h\nu \rightarrow S_x \rightarrow T_1 + h\nu \rightarrow T_x \rightarrow$ product), depending on the height of the barrier involved.[7–9]

So far, our calculations revealed two general cases where such phenomena are predicted for monomolecular electrocyclic reactions: first, those in which the orbital correlation resembles that in Figure 1 in that it is not the highest occupied molecular orbital of the reactant, but one of the more bonding ones, which becomes antibonding during the reaction (or similarly for the lowest free MO of the reactant or both). Typically, such reactions involve a drastic transformation of the chromophore, and barriers are present both in S_1 and T_1. In addition to I → II, another example for which such behavior is predicted is III → IV.[10] In the second case the orbital "crossover" is normal, but S_1 is not derived from the lowest energy configuration, $1 \rightarrow -1$. This situation arises commonly in aromatic chromophores as a result of strong configuration interaction between singlet $2 \rightarrow -1$ and $1 \rightarrow -2$ excitations. According to our calculations, such lowest singlet state ($2 \rightarrow -1$, $1 \rightarrow -2$, or ^1L_b in Platt's notation) typically correlates with a highly excited state of products. It is only the second singlet state, ^1L_a, which is of $1 \rightarrow -1$ character, that correlates smoothly with the first excited state of the product. The magnitude of the expected barrier for the reaction from S_1 depends on the separation between ^1L_b and ^1L_a. It is usually much smaller than the barrier found for cases such as I → II. For triplet states, the $1 \rightarrow -1$ (^3L_a) state is invariably below $1 \rightarrow -2$, $2 \rightarrow -1$ (^3L_b), and no barrier results.[11] Examples of such reactions are transformations of benzene and naphthalene chromophores into quinoid ones, such as V → VI, where disrotatory opening from S_1 should require "activation energy" (conrotatory opening is forbidden much more strongly yet and lacks the V–O minimum). So far, there seems to be no entirely conclusive experimental evidence to support such predictions. However, Becker, *et al.*,[12,13] have reported that the fluorescence quantum yield of several compounds with benzene or naphthalene chromophores which transform photochemically into quinoid derivatives decreases strongly with decreasing wavelength of exciting light, presumably because the photochemical process competes more efficiently.[14]

We are presently extending our calculations to new systems and searching for experimental evidence to verify our predictions. We hope that this communication will stimulate additional interest in this area.

Acknowledgment. I am very grateful to Professor F. E. Harris, University of Utah, who generously supported part of this work using funds from NSF Grant No. GP-11170.

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(7) When several competing reactions can occur, different product composition would be expected as wavelength of the exciting light or temperature is changed.

(8) The barriers for the processes A* → B and B* → A may be of unequal magnitudes; *e.g.*, the former may require two photons while the latter already proceeds from S_1 at elevated temperatures.

(9) Professor A. Weller suggested to us that two-photon reactions might also proceed in solution *via* triplet–triplet annihilation ($T_1 + T_1 \rightarrow S_x \rightarrow$ product).

(10) During the preparation of this manuscript, Professor J. Meinwald kindly communicated to us that he and his collaborators have indeed found III to behave as predicted[1] (submitted for publication).

(11) We believe that differences between singlet and triplet reactivities can be quite generally understood on the basis of differences in the shapes of potential energy surfaces of S_1 and T_1 due either to differences in configuration interaction, such as those discussed presently, or, more commonly, to the presence of V–O minima in the S_1 but not T_1 surface[3] (which in turn has minima corresponding to biradical structures). A more comprehensive communication on this topic is under preparation.

(12) R. S. Becker and J. Michl, *J. Amer. Chem. Soc.*, 88, 5931 (1966).

(13) R. S. Becker, E. Dolan, and D. E. Balke, *J. Chem. Phys.*, 50, 239 (1969).

(14) Another explanation of these results would be wavelength dependent rate of intersystem crossing followed by a reaction from the triplet state. Becker, *et al.*, consider this unlikely for systems such as the chromenes.[13] However, in other molecules, particularly those with relatively low-lying n–π* states, this may be an important source of wavelength dependence.

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Oxidation by Metal Salts. VII.[1] Syntheses Based on the Selective Oxidation of Organic Free Radicals

Sir:

We wish to report a novel reaction of enolizable ketones with olefins which takes place in the presence of metal oxidants such as manganese(III) and cerium(IV) acetates leading to the formation of γ-keto esters. This reaction, which depends on the selective ability of higher valent metal ions to oxidize organic free radicals, was in turn used to estimate the relative strengths of the various metal oxidants, Cu(II), Ce(IV), and Mn(III).

As a representative example, the reaction of acetone with octene-1 in the presence of manganic acetate under a nitrogen atmosphere was studied in detail. A solution of octene-1 (7.5 mmol), acetone (200 mmol), and manganic acetate (15 mmol) in glacial acetic acid (40 ml) containing 10% potassium acetate was heated at 85° until the brown manganic color had disappeared. Three major products were isolated after work-up: the saturated ketone undecanone-2 (1, 1.13 mmol); an unsaturated ketone[2] $C_{11}H_{20}O$ (II, 0.54 mmol), bp 79–81° (1.5 mm); and a keto acetate[3] $C_{13}H_{21}O_3$ (III, 1.78 mmol), bp 112° (1.0 mm). The relative yields of the three products could be changed by modifying the reaction conditions. The same products were ob-

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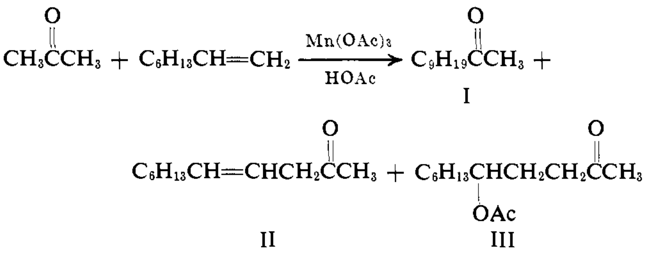
(1) Preceding paper by R. M. Dessau, S. Shih, and E. I. Heiba, *J. Amer. Chem. Soc.*, 92, 412 (1970).

(2) Probably a mixture of nonconjugated unsaturated ketones having ir absorption at 1727 cm^{-1} and a complex nmr multiplet in the τ 4.5–4.8 region.

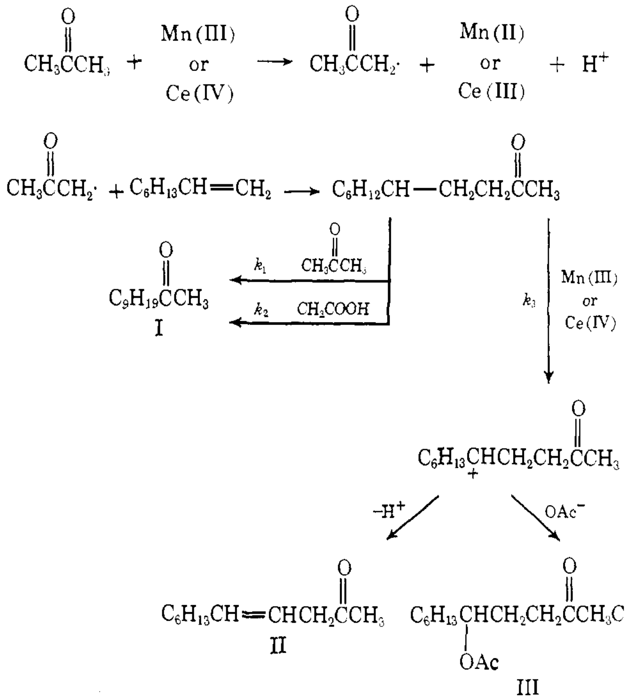
(3) The ir spectrum showed two carbonyl absorptions at 1742 and 1728 cm^{-1}, and the nmr spectrum was consistent with the assigned structure.



$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + C_6H_{13}CH{=}CH_2 \xrightarrow[HOAc]{Mn(OAc)_3} \underset{I}{C_9H_{19}\overset{O}{\overset{\|}{C}}CH_3} + \underset{II}{C_6H_{13}CH{=}CHCH_2\overset{O}{\overset{\|}{C}}CH_3} + \underset{III}{C_6H_{13}\underset{OAc}{\underset{|}{C}}HCH_2CH_2\overset{O}{\overset{\|}{C}}CH_3}$$

tained when ceric acetate was used in place of manganic acetate.

The formation of these products can best be explained by the mechanism shown below. In this mechanism, the initial step involves the oxidation of the ketone by either manganic or ceric ion leading to the α-keto radical.[4,5] This radical rapidly adds to the olefin forming a secondary alkyl radical which can either abstract hydrogen atoms from the solvent forming the saturated ketone I or be oxidized by the higher valent metal ion to the unsaturated ketone II and the keto acetate III.



The success of this reaction can be attributed to the very selective oxidation of organic radicals by metal ions. The initially formed α-keto radical is not easily oxidized due to the electron-withdrawing character of the carbonyl group,[6] whereas the secondary alkyl radical formed by addition to the olefin is quite readily oxidized by the metal ion.[7] The rapid oxidation of this adduct radical also accounts for the absence of significant polymerization during the course of the reaction. Other examples of syntheses based on the selective oxidation of carbon radicals include the Meerwein reaction,[8] the formation of lactones and alkyl ester adducts from olefins,[9] and the addition of free radicals to aromatic hydrocarbons.[10]

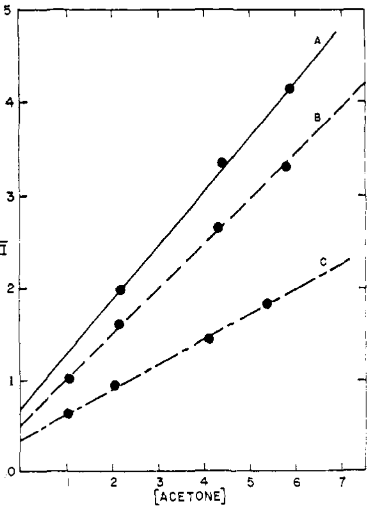


Figure 1. Effect of ketone concentration on product ratio: A, $[Mn(III)]_i = 8.34 \times 10^{-2} M$, $T = 45°$; B, $[Mn(III)]_i = 8.34 \times 10^{-2} M$, $T = 70°$; C, $[Mn(III)]_i = 1.67 \times 10^{-1} M$, $T = 70°$.

Applying a steady-state kinetic treatment to the mechanistic scheme shown above, one can derive the following equation, which predicts a linear relationship

$$\frac{d[I]}{d[II + III]} = \frac{k_1[CH_3COCH_3] + k_2[CH_3COOH]}{k_3[Mn(III)]}$$

between the product ratio and the acetone concentration. This was confirmed by experiments in which the acetone concentration was varied using benzene as diluent, as shown by the plots in Figure 1. Similar plots were also obtained using ceric acetate. From these plots, k_1 was found to be at least four times greater than k_2.

The ratio k_1/k_3, representing the rate constant of hydrogen abstraction from acetone relative to that of oxidation of the secondary alkyl radical by the metal acetate, could be derived from the slopes of these linear plots, assuming the oxidant concentration to be the average concentration during the course of the reaction; *i.e.*, $k_1/k_3 = \text{slope}[Mn(III)]_{av}$. Using manganic acetate, k_1/k_3 was found to be 2.20×10^{-2} at 70° and 2.62×10^{-2} at 45°, indicating an activation energy difference, $E_3 - E_1$, of 1.5 kcal/mol. With ceric acetate, k_1/k_3 was 1.85×10^{-3} at 67° and 1.58×10^{-3} at 45°, which corresponded to an activation energy difference, $E_3 - E_1$, of -1.5 kcal/mol.

In order to obtain more accurate values for the relative rates of radical oxidation by various metal acetates and to ensure the validity of using the average Mn(III) concentrations in the above equations, we studied the reaction under conditions where the Mn(III) concentration is kept relatively constant by stopping the reaction at relatively low conversions (10–30% reaction of Mn(III)). Plotting the ratio of the oxidation products II + III relative to the hydrogen abstraction product I *vs.* the Mn(III) concentrations yielded a linear plot (Figure 2), the slope of the line

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[4] R. VanHelden and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **80**, 57 (1961); H. J. den Hertog, Jr., and E. C. Kooyman, *J. Catal.*, **6**, 357 (1966).

[5] G. A. Russell and J. Lokensgard, *J. Amer. Chem. Soc.*, **89**, 5059 (1967).

[6] J. K. Kochi and D. M. Mog, *ibid.*, **87**, 522 (1965).

[7] J. K. Kochi, *Rec. Chem. Progr.*, **27**, 207 (1966).

[8] J. K. Kochi, *J. Amer. Chem. Soc.*, **79**, 2942 (1957).

[9] E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *ibid.*, **90**, 2706 5905 (1968).

[10] E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *ibid.*, **90**, 1082 (1968); **91**, 138 (1969).

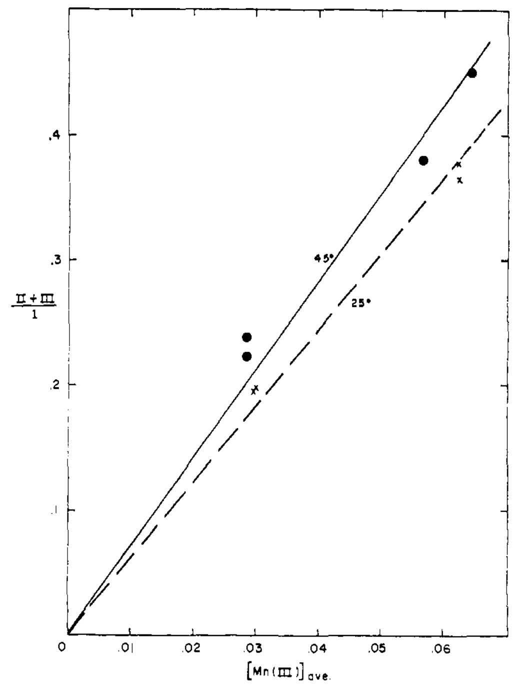

Figure 2. Effect of manganic ion concentration on product ratio.

($k_3/[k_1(CH_3COCH_3) + k_2(CH_3COOH)]$) being proportional to the rate constant for the oxidation of the secondary alkyl radical by Mn(III). Similar plots were obtained for Ce(IV). When the reactions were carried out at identical acetone and acetic acid concentrations, the ratio of the slopes obtained with Mn(III) and Ce(IV) yielded the relative rate constants for the oxidation of the secondary alkyl radicals by Mn(III) and Ce(IV) (Table I).

Table I. Comparison of Radical Oxidation by Mn(III), Ce(IV), and Cu(II)

Oxidant	Temp, °C	Slope[a]	Rel k_{oxid} (25°)	E_a[c]
Mn(III)	25	6.1	1	12.5
Mn(III)	45	7.1		
Ce(IV)	5	85		
Ce(IV)	25	74	12	9.5
Cu(II)	45	2,400	(350)[b]	
Cu(II)	68	2,800		12.5[d]

[a] All reactions were done under identical conditions, using the same concentrations of acetone and acetic acid. [b] Extrapolated value at 25°. [c] Assuming the activation energy for hydrogen abstraction by the secondary alkyl radical from acetone and acetic acid to be ~11 kcal/mol. [d] The lower apparent activation energies reported for the oxidation of primary alkyl radicals[11,13b] have been attributed to the reversible interaction of Cu(II) with the radicals and thus represent a minimum value. Our high value may be attributed to the relatively less reversible interaction of Cu(II) with secondary alkyl radicals in comparison with the interaction with primary alkyl radicals.[13b]

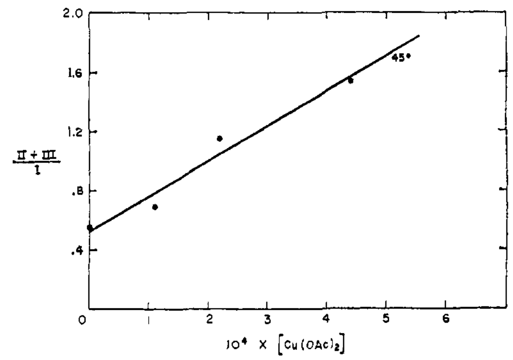

Figure 3. Effect of added cupric acetate on product ratio.

To compare the rates of radical oxidation by ceric and manganic acetates to that of cupric acetate, which is known to be extremely rapid,[11] the manganic acetate reaction was studied in the presence of added cupric acetate. In the presence of cupric acetate, the following relationship should be expected

$$\frac{d[II + III]}{d[I]} = \frac{k_3[Mn(III)] + k_4[Cu(II)]}{k_1[CH_3COCH_3] + k_2[CH_3COOH]}$$

where k_4 is the rate constant for the oxidation of the secondary alkyl radical by cupric ion, the concentration of which remains constant throughout the reaction. This was confirmed by the plot in Figure 3 which shows a linear dependence of the product ratio on the cupric acetate concentration.[12] From the ratio of the slopes of the plots in Figures 2 and 3, the relative radical oxidation rate constants were obtained (Table I).

From the data in Table I it can be seen that the order of the relative reactivity of the oxidation of secondary alkyl radicals by Mn(III), Ce(IV), and Cu(II) is of the order 1:12:350.[14]

The formation of α-keto radicals from enolizable ketones apparently involves attack of manganic acetate on either the enol or enolate anion. The rate of reaction of manganic ion with ketones was found to be independent of the manganic ion concentration,[15] first order in ketone concentration, and accelerated by acetate ions. In a study of the relative rates of disappearance of para-substituted benzyl phenyl ketones in the presence of manganic acetate, electron-withdrawing groups increased the reaction rates, as shown in Table II. A linear Hammett σ–ρ plot was obtained with a positive ρ of 0.8 (correlated with σ constants).[16]

Table II. Reactivity of Ketones toward Attack by $Mn(OAc)_3$ at 70°

Ketone	Rel reactivity
$C_6H_5CH_2COC_6H_5$	1.0
p-$MeC_6H_4CH_2COC_6H_5$	0.79
p-$ClC_6H_4CH_2COC_6H_5$	1.5
p-$BrC_6H_4CH_2COC_6H_5$	1.64
p-$NO_2C_6H_4CH_2COC_6H_5$	4.56

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(11) J. K. Kochi and R. V. Subramanian, *J. Amer. Chem. Soc.*, **87**, 4855 (1965).

(12) Apparently cupric acetate behaves as a monomer under our conditions as was the case in aqueous acetic acid.[11] In the presence of cupric acetate the ratio of unsaturated ketone to keto acetate is greatly increased, a phenomenon previously observed in the oxidation of alkyl radicals.[13]

(13) (a) J. K. Kochi and A. Bemis, *J. Amer. Chem. Soc.*, **90**, 4038 (1968); (b) J. K. Kochi, A. Bemis, and C. L. Jenkins, *ibid.*, **90**, 4616 (1968); (c) J. K. Kochi and J. D. Bacha, *J. Org. Chem.*, 33, 2746 (1968).

(14) Similar relative rates were observed by Professor J. K. Kochi in his work; private communication.

(15) A similar observation was reported for the manganese-catalyzed autoxidation of acetophenone.[4]

(16) V. G. Morgan and H. B. Watson, *J. Chem. Soc.*, 1173 (1935).

In accord with this interpretation, the major keto acetate product obtained from the reaction of methyl isopropyl ketone with octene-1 [$C_6H_{13}CH(OAc)CH_2CH_2COCH(CH_3)_2$] derived from the primary α-keto radical rather than the more stable tertiary keto radical.

The selective oxidation of organic free radicals provides novel approaches to organic synthesis. Further examples will be presented in a forthcoming publication.

Acknowledgment. The authors are indebted to Mr. G. E. Stead for his skillful technical assistance in carrying out the reported experiments.

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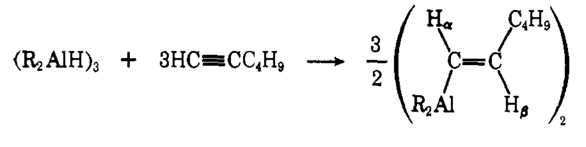
Mixed Alkenyl–Hydride-Bridged Alkylaluminum Dimers. Intermediates in the Monohydroalumination of Alkynes[1]

Sir:

The monohydroalumination of alkynes with dialkylaluminum hydrides proceeds *via* a cis addition of Al–H to the triple bond to afford dialkylalkenylalanes of predictable stereochemistry.[2] It has been established



that these dialkylalkenylalanes form stable vinyl-bridged dimers which do not dissociate when heated below 100°.[3] We now wish to present evidence for the formation of mixed alkenyl–hydride-bridged alane dimers, a new class of dimeric organoaluminum compounds, as stable intermediates during the monohydroalumination of various alkynes. This evidence was obtained by following the changes in the vinyl proton region of the 60-MHz nmr spectra of the reaction mixtures during the course of the hydroalumination reactions.

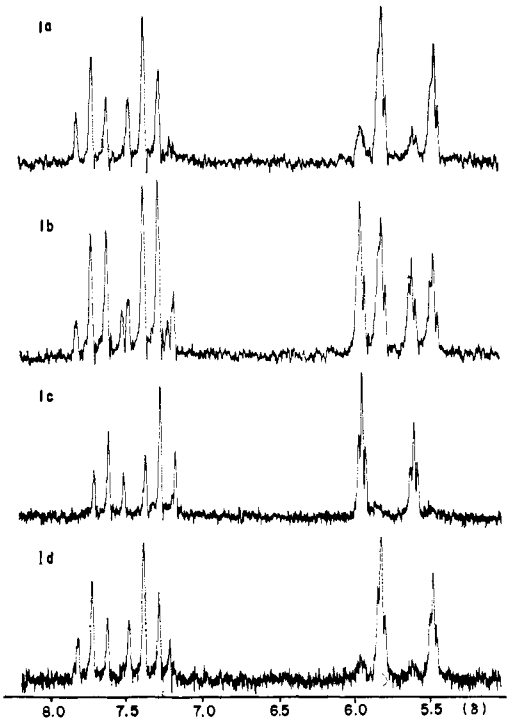


Figure 1. Vinyl proton region of the nmr spectrum of solutions of diisobutylaluminum hydride and 1-hexyne at 25°: (a) 47% reaction (15 min), (b) 67% reaction (45 min), (c) after complete reaction (25 hr), (d) sample used in (c) with 1.5 equiv of diisobutylaluminum hydride added.

To a solution of 1-hexyne in *n*-hexane was added at 25° an equimolar amount of diisobutylaluminum hydride.[4] A portion of the reaction mixture was placed into an nmr tube. After 47% reaction the nmr spectrum (Figure 1a) exhibited primarily two separate doublets of triplets centered at δ 7.55 and 5.49 ppm, resulting from the β- and α-alkenyl protons, respectively. As the reaction progressed, the β-proton resonances changed to what appeared to be a doublet of quartets, whereas two sets of doublets of triplets were observed in the α-proton region (Figure 1b). Finally, when all of the available hydride was utilized the spectrum of the resultant diisobutyl(*trans*-1-hexen-1-yl)alane exhibited doublets of triplets both at δ 7.42 and 5.75 ppm, attributed to the β- and α-alkenyl protons, respectively (Figure 1c). It is apparent that the spectrum of Figure 1b results from superposition of the resonance signals observed in the spectra of Figures 1a and 1c. Moreover, it is important to note here that the spectrum in Figure 1a can be replicated by adding an excess of diisobutylaluminum hydride to diisobutyl(*trans*-1-hexen-1-yl)alane. It should also be noted that exchange of vinyl and of hydride bridging groups is slow on the nmr time scale. Separate signals, rather than time averaged signals, are observed for the vinyl groups of complexes I and II. When excess diisobutylaluminum hydride is added to complex II, two types of hydride resonance signals are observed.

The observed changes in the nmr spectra with increasing reaction time are compatible with the formation of a complex between the alkenylalane and excess diisobutylaluminum hydride.[5] Further reaction of the complex with remaining alkyne affords the diisobutyl(*trans*-1-hexen-1-yl)alane dimer. Based on the nmr

$$^4/_3(R_2AlH)_3 + 2HC{\equiv}CC_4H_9 \longrightarrow$$
$$2R_2AlH\cdot R_2AlCH{=}CHC_4H_9 \underset{(R_2AlH)_3}{\overset{HC\equiv CC_4H_9}{\rightleftarrows}} (R_2AlCH{=}CHC_4H_9)_2$$

data and cryoscopic molecular weight determinations,[6] we propose structure I for the dialkylalkenylalane

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[1] This research was supported by Grant No. GP-9398 from the National Science Foundation.

[2] G. Wilke and H. Müller, *Justus Liebigs Ann. Chem.*, **629**, 222 (1960).

[3] R. Köster and P. Binger, *Advan. Inorg. Chem. Radiochem.*, 7, 274 (1965).

[4] Diisobutylaluminum hydride is trimeric in benzene solution: K. Ziegler, W. R. Kroll, W. Larbig, and O. W. Steudel, *Justus Liebigs Ann. Chem.*, **629**, 53 (1960); E. G. Hoffmann, *ibid.*, **629**, 104 (1960).

[5] The spectra also reveal that the resonance signal for the hydride in the complex (δ 3.75) is downfield from that for the hydride in the diisobutylaluminum hydride (δ 2.9).

[6] Molecular weights were determined by freezing point depression measurements of 0.01–0.03 *m* solutions in benzene. Molecular weights obtained (calculated values in parentheses) were: *I*, 463 (448); II, 414 (366). The fact that the molecular weight of II differs from the theoretical value by more than the experimental error (±5%) suggests that the complex is partially dissociated.